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	The PbF A($\Omega=\frac{1}{2}$) - X ² II, band system has been vibrationally reanalysed, based on the observation of 69 new bandheads. The singlet-triplet splitting in methylege (CH ₂)			
لبا	has been estimated to be 8.1±0.8 kcal/mole, based	on the detect	ion of CH ₂ A ₁	٦
	following the photolysis of ketene (CH_2CO) . The b SF have been determined to be $72.9\pm2,^291.1\pm3.2$, a	and energies	of Bal, SFil and cal/mole, Based or	
	the appearance of chemiluminescent reactions with	metastable al	kaline earth atoms	
	The two CioHa isomers, azulene and naphthalene, ha spectrometer through the use of laser-controlled m	ve been disti	nguished in a mass	-
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METAL COMBUSTION PROCESSES AS STUDIED BY
CHEMILUMINESCENCE AND CHEMI-IONIZATION.

(10) RICHARD N./ZARE

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U. S. ARMY RESEARCH OFFICE

CONTRACT NUMBER DAAG 29-77-G-0151

LELAND STANFORD JUNIOR UNIVERSITY

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FINAL REPORT

"Metal Combustion Processes as Studied by Chemiluminescence and Chemi-ionization"

Contract Number:

DAAG 29-77-G-0151

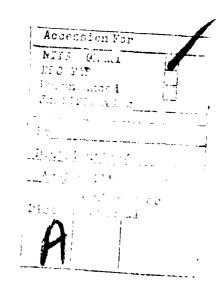
Period:

July 1, 1977 - February 1, 1980

Name of Institution: Leland Stanford Junior University

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Summary of Research Highlights

The reaction Pb + F_2 has been studied under beam-gas conditions at F_2 pressures of 10^{-4} torr and in the presence of argon at ~7 torr. A series of 133 red degraded bandheads belonging to the $A(\Omega=\frac{1}{2})-X^2\Pi_{\frac{1}{2}}$ band system are observed; 69 of these bandheads are new and a vibrational reanalysis is made. The PbF A state is thought to be populated by the reaction of a metastable lead atom $Pb(^3P_1)$ of $Pb(^3P_2)$ with nolecular fluorine.

By photodissociating ketene ($\mathrm{CH_2CO}$) in the 3400-2900 Å region, singlet methylene ($\mathrm{CH_2}^1\mathrm{A_1}$) is detected by laser-induced fluorescence by observing the $\mathrm{CH_2}^1\mathrm{B_1}^{-1}\mathrm{A_1}$ red band system. Under collision-free conditions a study of the appearance of $\mathrm{CH_2}^1\mathrm{A_1}(0,0,0)$ as a function of photodissociation wavelength and as a function of ketene temperature leads to a value for the heat of formation of singlet methylene:

$$\Delta H_{f0}^{0}(CH_{2}^{1}A_{1}) = 101.7 \pm 0.5 \text{ kcal/mole}$$

When this is combined with other known heats of formation, the singlet-triplet splitting is estimated to be 8.1 ± 0.8 kcal/mole, in good agreement with the most recent ab initio calculations of this quantity.

During this contract period we have constructed a pulsed source of metastable alkaline earth atoms, particularly $Ba(^3D)$, $Ca(^3P)$, and $Sr(^3P)$. The metastable atoms traverse a scattering chamber filled with oxidant gas at low pressure (beam + gas arrangement) and the resulting chemiluminescence is analyzed

spectroscopically and as a function of the time elapsed between the formation of the metastables and the appearance of the chemiluminescence in the reaction/observation zone. This information is combined with known thermodynamic data to determine the bond energy of the gas molecule under study. In this manner we have found that

$$D_0^0(BaI) = 72.9 \pm 2$$
 kcal/mole
 $D_0^0(F_5S-F) = 91.1 \pm 3.2$ kcal/mole
 $D_0^0(F_3S-F) = 84.1 \pm 3.0$ kcal/mole

The latter two quantities may be combined with existing data to deduce the stepwise bond dissociation energies of SF_{δ} . A zigzag pattern appears in which the magnitude of the bond energy is larger for the even members. This behavior can be rationalized by a simple model which involves transformation of lone pair electrons on the central sulfur atom at first to a weak two-center three-electron bond and then to a strong three-center four-electron bond.

The possible use of laser ionization as an analytical detecter has been explored by demonstrating the facile detection of the two $C_{10}H_8$ isomers, azulene and naphthalene. Compared to electron impact, multiplication ionization provides rore gentle ionization at low laser power and more extensive fragmentation at high laser power. Moreover, the efficiency of the latter exceeds that of the former during the time the laser is on. It would appear that this technique should make a useful addition to mass spectrometry.

Publications Supported Under DAAG 29-77-6-0157

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- D. M. Lubman, R. Naaman, and R. N. Zare, "Multiplication Ionization of Azulene and Naphthalene," J. Chem. Phys. (accepted for publication).

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